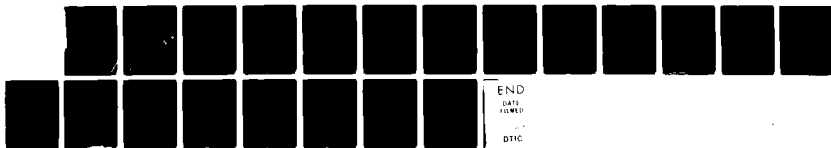
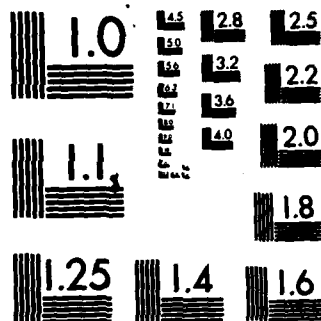


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Characterization of Polypyrrole

by

G. B. Street, T. C. Clarke, R. H. Geiss, V. Y. Lee,

A. Nazzal, P. Pfluger, and J. C. Scott

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IBM Research Laboratory  
5600 Cottle Rd.  
San Jose, CA 95193

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# Research Report

## CHARACTERIZATION OF POLYPYRROLE

G. B. Street  
T. C. Clarke  
R. H. Geiss  
V. Y. Lee  
A. Nazzari  
P. Pfluger  
J. C. Scott

IBM Research Laboratory  
San Jose, California 95193

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## CHARACTERIZATION OF POLYPYRROLE

G. B. Street  
T. C. Clarke  
R. H. Geiss  
V. Y. Lee  
A. Nazzari  
P. Pfluger\*  
J. C. Scott

IBM Research Laboratory  
San Jose, California 95193

*beta prime*  
**ABSTRACT:** Using  $\beta,\beta'$ -dimethylpyrrole polymers to reduce the structural disorder it has been possible to interpret the results of electron diffraction data and to propose an idealized structure for neutral polypyrrole. XPS data have been used to define some of the deviations from this ideal structure that are seen in actual films and the origin of some of these defects is related to the mechanism of polymerization. The planarity of the chain structure is shown to be important for high conductivity in pyrrole polymers which appears to involve spinless carriers perhaps associated with bipolarons. ←

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\*Now at Brown Boveri Research Center, CH-5405 Baden, Switzerland.

## INTRODUCTION

Pyrrole blacks have been known since 1916<sup>1</sup> when they were first obtained as powders by chemical oxidation of pyrrole monomer. These insoluble polymers have not been characterized in great detail though they are known to be polymers of pyrrole where the bonding is predominantly via the  $\alpha, \alpha'$  carbons. It was not until 1968<sup>2</sup> that films of these materials were first made by the electrochemical oxidation of pyrrole. In 1979,<sup>3</sup> an improved electrochemical technique was used to prepare free standing films with sufficiently good mechanical properties to make practical the investigation of this system as a conducting polymer. Polypyrrole has been particularly difficult to characterize because no solvent has been found and because it is extremely poorly crystalline such that no information is obtainable from x-ray studies. The limited structural data that has been available has come by taking advantage of the selective area capabilities of electron diffraction. A further problem with this polymer was its stoichiometry which until recently was poorly defined. Although the polymer was shown to be predominantly bonded via the  $\alpha, \alpha'$  carbons of the pyrrole rings, the presence of other types of linking not only led to disorder in the polymer but also tended to confuse the interpretation of much of the characterization data.<sup>4</sup> In order to resolve some of these problems and facilitate characterization, polymers have been synthesized in which both the  $\beta$  positions of the pyrrole ring are blocked to ensure exclusive  $\alpha, \alpha'$  bonding of the polymer chain. In the case of the  $\beta, \beta'$  dimethyl pyrrole, this leads to an increased chain order which in turn results in significant improvement in the crystallinity of the polymer, enabling a model for the structure of polypyrrole to be described in this paper. The role of chain planarity and the hydrogen on the nitrogen in determining the conductivity will be discussed together with the present knowledge of the chain length and conjugation length of the polymer. All the films described in this work were prepared using the dry box

techniques described in our previous paper.<sup>4</sup> This was done to simplify the interpretation of the characterization data by avoiding contamination of the films by oxygen or moisture.

## ELECTROCHEMICAL POLYMERIZATION OF PYRROLE

The first step in the electrochemical polymerization of pyrrole is the generation of the radical cation at the anode as shown in Fig. 1. Chain propagation may then proceed by reaction of two radical cations, pairing the spins and eliminating two protons to produce the neutral dimer. The elimination of the protons is confirmed by the slow rise in the pH of the electrolyte solution during film growth. At the potentials necessary to oxidize the monomer presumably the dimer and higher oligomers are also oxidized to the corresponding radical cation. Chain propagation continues by reaction of the oligomer radical cation primarily with the radical cation of the monomer, which is present in high concentration in the region of the anode. As the chain grows the pyrrole oligomer becomes insoluble and eventually precipitates out on the electrode, where the chain can continue to grow until the oligomer radical cation becomes too unreactive or until it becomes prevented from reacting by steric reasons.

Elemental analysis reveals that the situation is more complex than this simple mechanism would indicate. Additional oxidation of the polypyrrole chain leads to the formation of cationic sites with incorporation of the electrolyte anion to maintain charge neutrality. Results on both polypyrrole and poly  $\beta,\beta'$ -dimethylpyrrole (PBDMP) perchlorates indicate the presence of one perchlorate for every three pyrrole rings. However, these analyses also reveal that, on the average, for every three pyrrole rings there is one more hydrogen than the idealized structure would indicate. Although the amounts of hydrogen and perchlorate are almost identical, spectroscopic data indicate that these species are not present in the form of perchloric acid. Indeed, infrared<sup>4</sup> and <sup>13</sup>C NMR studies<sup>5</sup> in the presence of

$sp^3$  C-H moieties in polypyrrole, perhaps arising from the addition of hydrogen to the pyrrole ring under the acidic conditions of the electrochemical polymerization.<sup>6</sup> In addition, chain ends would contribute to the excess hydrogen observed in the elemental analysis.

Because the excess hydrogen may be distributed among several different types of sites, the elemental analysis data cannot be used to derive either chain length or conjugation length. However, certain limits can be placed on these parameters. Thus, if all of the excess hydrogen were present at chain ends, the data would indicate a chain length of 7 to 8 pyrrole rings; the presence of hydrogen at internal chain sites makes this a lower limit on the chain length. The effects of the  $sp^3$  hydrogen depends on their currently unknown distribution between  $\alpha$  and  $\beta$  sites. Hydrogen at an  $\alpha$  pyrrole carbon definitely interrupts the  $\pi$ -conjugation along the polymer backbone, whereas substitution at a  $\beta$  carbon may not. If the excess hydrogen were all at  $\alpha$  sites, the average conjugation length would be on the order of three pyrrole rings; in fact the presence of hydrogen at other positions makes this a lower limit on the conjugation length.

The possibility of a very short conjugation length in polypyrrole is difficult to reconcile with the observation of a single oxidation peak in cyclic voltammetry unless a single conjugation length dominates the distribution. Also, extrapolations of electrochemical potentials and optical data for short chain pyrrole oligomers suggest a conjugation length on the order of six or more pyrrole rings.<sup>7</sup> Moreover, EPR results indicate only one spin for every 50 pyrrole rings.<sup>8</sup> Single oxidation of a given conjugated segment would result in a polaron state (a radical cation) with an unpaired spin. Thus, the conjugation length must be long enough to support doubly oxidized states (bipolarons) which do not contain unpaired spins. In conjunction with the elemental analysis data indicating one perchlorate, and thus one charge, per three pyrrole rings, a lower limit on the conjugation length of six rings would



be indicated. To be consistent with the cyclic voltammetry, however, this model requires that the first and second oxidation potentials for a conjugated segment fall within the same envelope.

### $\beta,\beta'$ SUBSTITUTED PYRROLE POLYMERS

The  $\beta,\beta'$  dimethyl pyrrole monomer can be polymerized to give films of very similar appearance to regular polypyrrole. The oxidation potential of the monomer is +1.0 relative to SSC electrode as shown in Table 1. This oxidation potential is lower than that of pyrrole monomer itself, presumably due to the effect of the methyl groups. The conductivity of the films of PBDMP is about  $10 \text{ ohm}^{-1}\text{-cm}^{-1}$ , a factor of four less than that of PP itself. Thus the conductivity of the PBDMP is similar to that of the mono  $\beta$  methyl pyrrole polymer.<sup>9</sup> By contrast the conductivity of the  $\beta,\beta'$  diphenyl pyrrole is some four orders of magnitude less,  $10^{-3} \text{ ohm}^{-1}\text{-cm}^{-1}$  which is very similar to the conductivity of poly-N-methylpyrrole.<sup>10</sup> Models indicate that the three highly conducting pyrrole polymers in Table 1 can all be planar whereas both the low conductivity polymers cannot be planar. This data seems to support the idea that polymer chain planarity is important for high conductivity which is consistent with the basic premise of a delocalized  $\pi$  system. It is also interesting to note that the redox potentials of the three highly conducting, planar polymers are all of a similar negative potential while the two poorly conducting nonplanar systems have positive redox potentials of 0.5 volts versus SSC. It has frequently been suggested that the hydrogen on the nitrogen was somehow important in the conductivity process.<sup>11</sup> These data clearly show that the presence of such a hydrogen does not convey conductivity on a polymer system which is not planar as seen from the case of the diphenyl substituted polymer. On the other hand, in the absence of a hydrogen on the nitrogen, the polymer cannot be planar and therefore cannot be highly conducting. However the question of whether the hydrogen plays a more

active role remains to be answered, though XPS data<sup>12,13</sup> certainly have been interpreted in terms of a labile NH group in polypyrrole. Similar conclusions as to the importance of planarity for high conductivity can also be obtained from a study of substituted polythiophenes which of course have no hydrogen attached to the heteroatom. Table 2 shows the conductivity of several polythiophenes and the corresponding pyrroles. It should be pointed out that the pyrrole polymers contain more anions, 1 per 3 rings, than the thiophenes, 1 per 7 rings.<sup>14</sup> However, the anion was bivalent ( $\text{SO}_4^{2-}$ ) in the latter case so the degree of oxidation of both polymers is similar. These differences may partly explain the 3 orders of magnitude lower conductivity of polythiophene relative to the polypyrrole. However the demonstrated sensitivity of the conductivity of chemically polymerized thiophenes to small amounts of non- $\alpha, \alpha'$  linkages<sup>15</sup> suggests that such linkages may also be important in electrochemically prepared polymer. This would be consistent with the higher conductivity measured for the mono  $\beta$  methyl thiophene polymer which [16] should contain fewer of these linkages. Eliminating these linkages entirely, by going to the  $\beta, \beta'$  dimethyl thiophene ought to lead to an even higher conductivity. However as shown in Table 2, the reverse is actually observed and blocking the beta positions leads to a polymer of lower conductivity. The reasons for this are made very clear from molecular models which show that the dimethyl substituted polymer cannot be planar.

## STRUCTURAL MODEL FOR PYRROLE POLYMERS

It is usually assumed in an ideal polypyrrole, ignoring the presence of excess hydrogen and non  $\alpha, \alpha'$  bonding, that the pyrrole rings alternate as shown in Fig. 2. This arrangement is required if the chain is to be linear. Otherwise, the pyrroles could form either a planar ring structure comprised of 10 pyrrole rings with the nitrogen of each pyrrole pointing to the center of the ring or a spiral arrangement. Although we do not believe that either of these

structures plays an important role in polypyrrole it does seem likely that the failure of adjacent rings to alternate could be an important source of defects. These defects would give rise to bends in the chain. Such defects are much more sterically hindered in the case of PBDMP. This, coupled with the fact that PBDMP is exclusively  $\alpha, \alpha'$  bonded, no doubt plays a part in enhancing the order of this polymer relative to polypyrrole itself. This increased order is reflected in ESR, NMR, XPS, and electron diffraction studies. Models of PBDMP suggest that it is possible to form a flat linear chain. Electron diffraction patterns<sup>17</sup> from planar specimens show a few diffuse maxima in the case of neutral polypyrrole while patterns from planar specimens of PBDMP contain more maxima and with some displaying texture suggesting a preferred orientation of the chains parallel to the plane of the film. It is believed that in both cases the polypyrrole chains lie with the pyrrole rings coplanar with the film surface. From the diffuseness of the diffraction patterns it is clear that both materials are very poorly crystalline. The observed diffraction maxima come from small crystalline regions separated by much larger amorphous regions. In the case of regular polypyrrole, these crystalline regions are randomly oriented with respect to each other, whereas the arcing of the pattern for the PBDMP suggests that the crystalline regions are aligned with one another. From diffraction patterns of cross sections of films it is possible to identify the spacings corresponding to the separation between the planes of chains. In polypyrrole this distance is  $3.41 \text{ \AA}$ , very close to the basal spacing in graphite, indicating that the separation between chains is determined by the  $\pi, \pi$  interaction of the pyrrole rings. In PBDMP the separation between chains is affected by the methyl groups and the interplanar spacing increases to  $3.65 \text{ \AA}$ . If the ideal polypyrrole chain is indeed linear and planar, and if the dimensions of the pyrrole ring do not change significantly from those of the monomer, it is possible to determine the chain geometry by assuming the value for the pyrrole, pyrrole bond to be that measured for the ring, ring bond in polyphenylene. These assumptions give rise to

the geometry shown below with the translation vector along the chain of  $7.35\text{\AA}$ . Using this chain geometry it has been possible to model a structure which is consistent with all the observed spacings from the diffraction studies. For neutral polypyrrole the proposed packing consists of planes of chains arranged as shown in Fig. 3 and stacked on top of one another in an abab... sequence to give a monoclinic structure with lattice constants  $a=8.2\text{\AA}$ ,  $b=7.35\text{\AA}$ ,  $c=6.82\text{\AA}$ ,  $\alpha=\beta=90^\circ$ , and  $\gamma=117^\circ$ . In the oxidized conducting form of the polymer the anions do not intercalate between the planes of the chains but instead appear to intercalate between the chains within the plane. This arrangement has some important consequences, because for large anions the structure will be determined by the packing of the anions and the resulting structures will probably have very little relation to the structure proposed above. Large anions intercalating in this fashion will also tend to isolate the polymer chains leading to reduced interchain coupling and adversely affecting the conductivity. Preliminary attempts to grow polypyrrole with tetraphenyl borate or stearate anions, led to very low conductivity ( $<10^{-3}\text{ohm}^{-1}\text{-cm}^{-1}$ ) films.

### STRUCTURAL DISORDER IN POLYPYRROLE

In the previous section, though mention was made of structural disorder, an ideal chain geometry was assumed to model the polymer crystal structure. In actual films, there are gross deviations from this ideal chain structure, revealed by many techniques including  $\text{C}^{13}\text{NMR}$  studies and more specifically XPS studies. The  $\text{C}1\text{s}$  spectrum for polypyrrole perchlorate is shown in Fig. 4. The spectrum consists of one broad peak centered at  $284.2\text{ eV}$  with a FWHM of  $2.2\text{ eV}$ . Though the peak is broad and asymmetric the  $\alpha$  and  $\beta$  carbons are not resolved as they are in the monomer. Lineshape analysis shows that this asymmetric peak can be fitted by 3 peaks. The two lowest energy peaks are centered at  $283.6\text{ eV}$  and  $284.5\text{ eV}$ . These two peaks are believed to be associated with the  $\alpha$  and  $\beta$

carbons and their splitting is 0.9 eV as observed in the monomer. The third peak centered at 285.4 eV is very broad with a FWHM of 2.4 eV and is believed to result from the non-ideal  $\alpha$  carbons, *e.g.*, those associated with chain ends, those which are non- $\alpha, \alpha'$  bonded, and those in partially saturated rings. The intensity of the  $\alpha$  and  $\beta$  peaks should be the same. However the  $\alpha$  peak and the disorder peak probably gain some intensity from hydrocarbon impurities present in almost any XPS spectrum in the region  $\sim 284.5$ –285 eV. Even after reducing the  $\alpha$  and the disorder peaks by an appropriate factor, such as to equalize the intensity of the  $\alpha$  and  $\beta$  peaks, the remaining intensity in the disorder peak implies that as many as 1/3 of the pyrrole rings are affected by structural disorder. The enhanced order of the PBDMP films is clearly shown in the XPS data by the linewidths of its C1s signal which is reduced to a FWHM of 1.7 eV compared to 2.2 eV for polypyrrole itself. In addition, there is much less asymmetry on the high binding energy side consistent with a reduction in the disorder peak.

#### STABILITY OF POLYPYRROLE

An attractive feature of the oxidized conducting form of polypyrrole is its stability in air relative to many other conducting polymers. The conductivity of films which have been exposed to air for a period of a year decreases only by about 20%. Although exposing the films to ammonia gas causes an order of magnitude decrease in the conductivity, exposure to concentrated sulfuric acid for 12 hours does not seem to adversely affect the films. On the other hand the neutral insulating form of the polymer is extremely unstable. In fact it may only be maintained in the neutral state when in contact with the reducing agent *e.g.*, sodium naphthalide solution or cesium vapor, used to effect its reduction from the oxidized state. The reactivity of the neutral form of the polymer may be partly responsible for the changes in the polymer which takes place on electrochemical cycling, particularly the loss of the anion

originally incorporated into the film from the electrolyte salt. The other consequence of electrochemical cycling is the elimination of the free spins present initially in the as grown films. The absence of an epr signal in the conducting form of the polypyrrole after cycling<sup>8</sup> strongly suggests that the conductivity is occurring via a mechanism involving bipolarons. The possible importance of polarons in polypyrrole was mentioned previously by Brazovskii and Kirova<sup>18</sup> Such a mechanism has been discussed previously for polyparaphenylene<sup>19</sup> which in common with polypyrrole also has a nondegenerate ground state.

#### ACKNOWLEDGMENTS

We thank J. Bargon for some stimulating discussions on the nature of the polymerization of pyrrole and we thank the Office of Naval Research for partial support of this work.

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### Mechanism of Formation of Polypyrrole

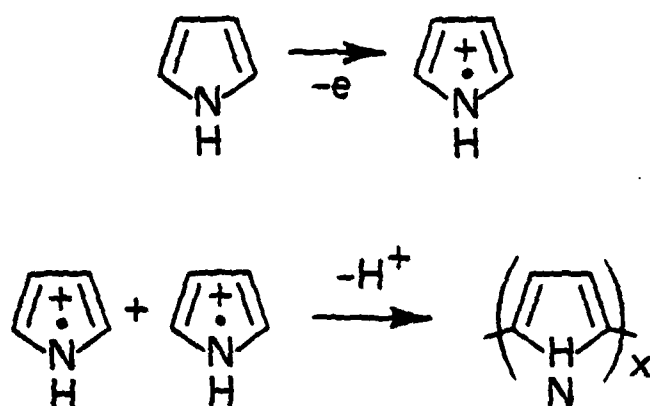


Figure 1. Formation and polymerization of the pyrrole radical cation.

## Chain Structure of Polypyrrole

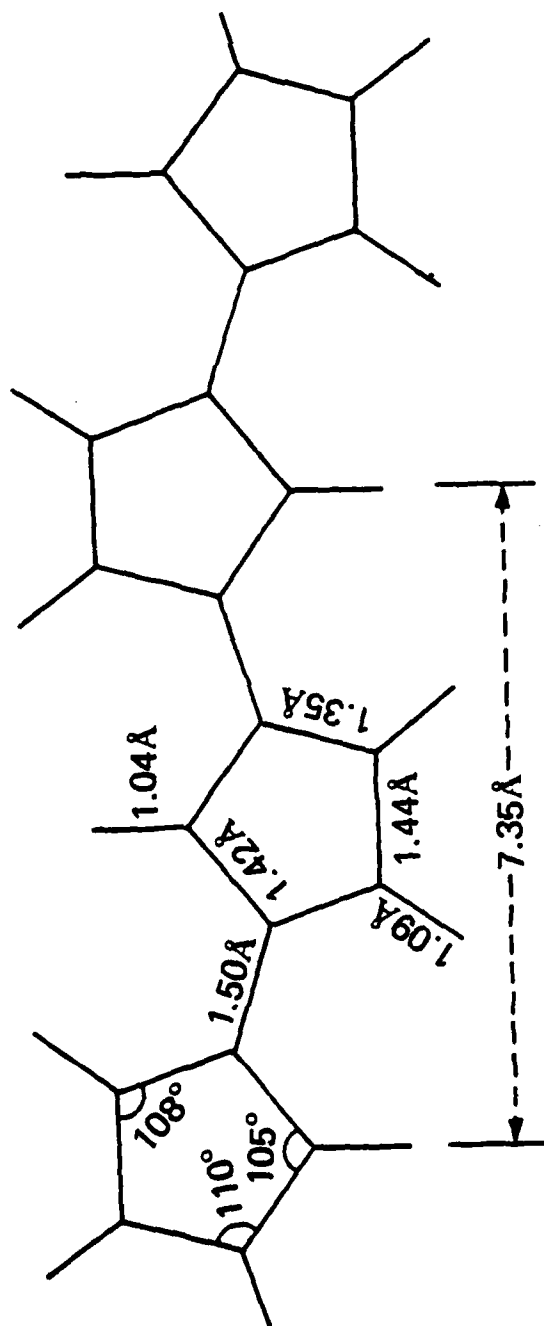
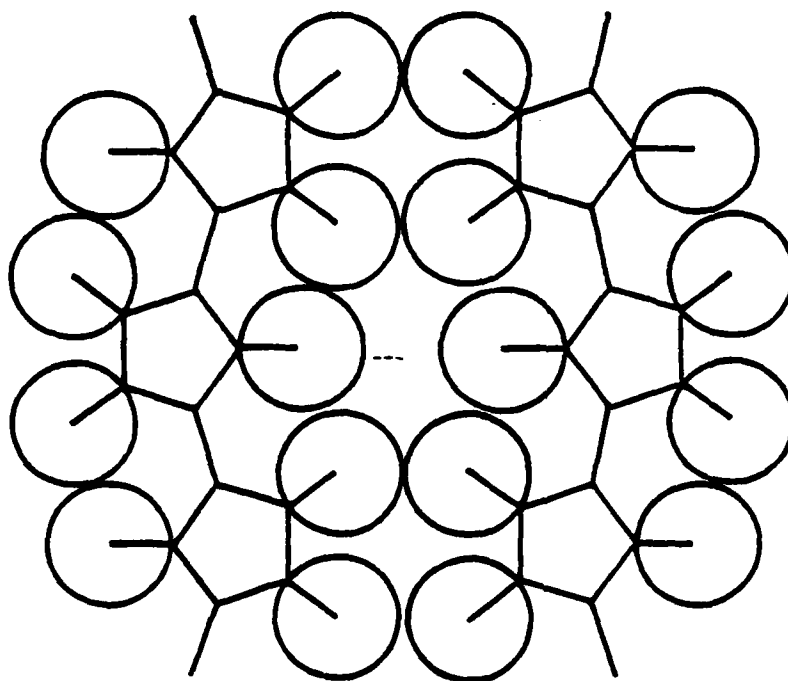


Figure 2. Chain structure of neutral polypyrrole.



**Figure 3.** Arrangement of chains in neutral polypyrrole. The circles represent the VDW diameters of the hydrogens.

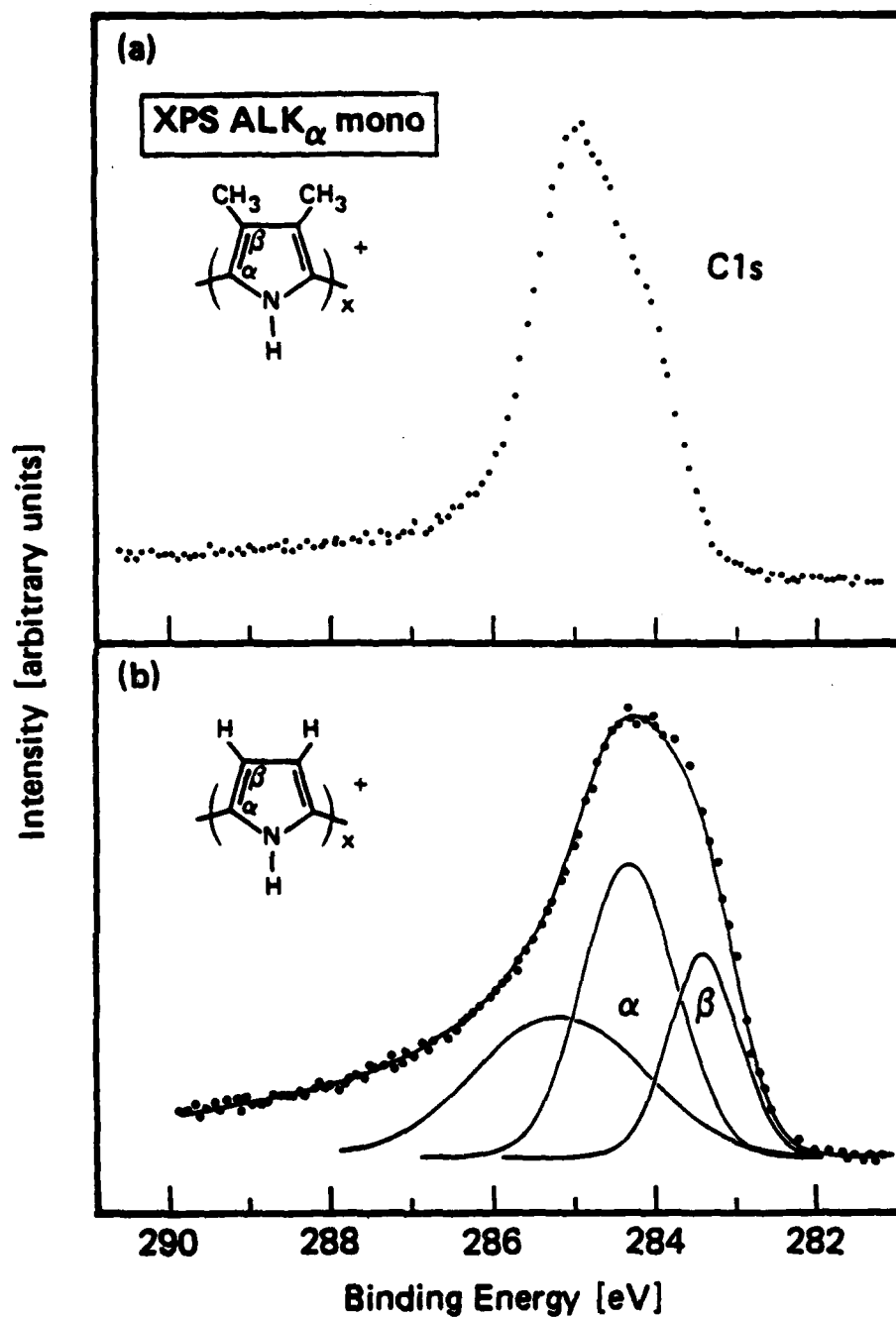


Figure 4. C1s XPS core level spectrum of polypyrrole perchlorate. The lower lines show the contributions from  $\alpha$ ,  $\beta$ , and disorder type carbons.

## Heterocyclic Polymers

## Polypyrroles

## Polythiophenes

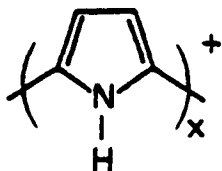
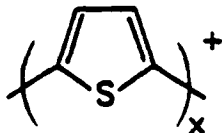
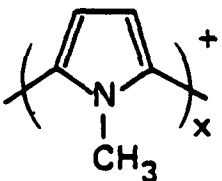
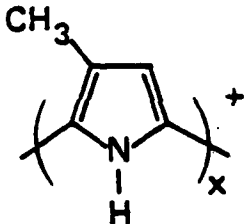
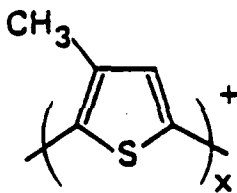
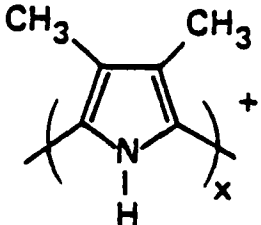
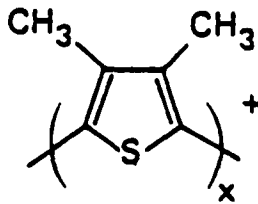
	Conductivity- $\Omega^{-1} \text{ cm}^{-1}$		Conductivity $\Omega^{-1} \text{ cm}^{-1}$
	40		$10^{-2}$
	$10^{-3}$		
	4		1
	10		$10^{-3}$

Table 1. Conductivity and electrochemistry of pyrrole polymers.

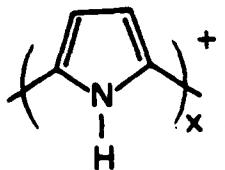
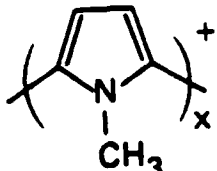
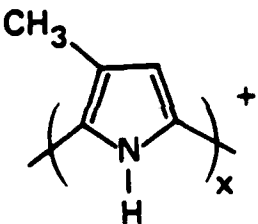
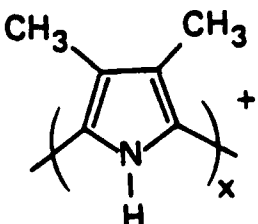
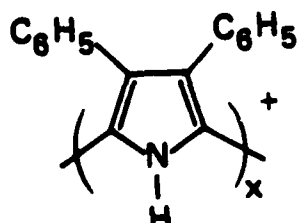
	Polypyrrole		Monomer
	Conductivity $\Omega^{-1} \text{ cm}^{-1}$	Redox Potential Volts	Oxidation Potential Volts
	40	-0.2	+1.2
	$10^{-3}$	+0.5	+1.2
	4	-0.3	
	10	-0.1	+1.0
	$10^{-3}$	+0.5	+1.2

Table 2. Conductivity of pyrrole and thiophene polymers.